

PROCESS FOR REMOVING OIL-BASED COMPONENTS AND FORMING CERAMIC BODIES

[0001] This application claims the benefit of U.S. Provisional Application No. 60/422,191, filed 10/29/02, entitled "Process for Removing Oil-Based Components and Forming Ceramic Bodies", by Y. F. Chan et al.

BACKGROUND OF THE INVENTION

[0002] The instant invention relates to an improvement in a process of forming ceramic multicellular articles. More particularly, the present invention relates to removal of oil-based components from shaped green ceramic articles after drying and before firing to avoid uncontrolled burning and hazardous conditions during manufacturing, and an apparatus for carrying out the same.

[0003] Popular ceramic multicellular ceramic bodies which are generally formed by extrusion, such as those finding applications in catalytic converters, diesel particulate filters, electrically heated catalysts, and chemical processing, require binders and extrusion aids for proper processing. Typically, water-soluble cellulose ether binders are used; however, such binders alone are not suitable for the manufacture of high cell density cellular structures having a large frontal area and extremely thin walls of less than webs of 0.002 inch (0.048 mm) or less. U.S. Pat. Nos. 6,080,345 and 6,368,992 disclose the use of oils or oil-based compounds, such as polyalphaolefin, in combination with cellulose ether binders for improved processing of such structures.

[0004] While advantageous in providing shape retention for very thin-wall ceramics in the wet green strength, oils lead to significant problems during firing. Specifically, such compounds release small volatile combustibles when heated, which unless controlled effectively can lead not only to cracking of the structural bodies, but also to uncontrolled combustion, or detonation in the kiln. At temperatures above their flash points, the oils decompose quickly and lead to sudden thermal stresses which may increase the risk of cracking in the ceramic articles.

[0005] Removal of the organic compounds during firing comprises a sequence of simultaneous reactions which are fairly complex, including, for example, oxidation,

volatilization, and thermal degradation. Therefore, it is difficult to remove the organic components from the shaped green ceramic article without incurring distortion or breakage of the part.

[0006] Because of the reduced strength of the very twin-wall ceramic honeycomb substrates, and the corresponding increase in the dimensional changes due to the exothermic nature of the removal of the organic compounds, special consideration in the firing must be undertaken to avoid cracking of the ceramic body. Specially designed kilns, apparatus for volatile removal, reduced oxygen containing atmospheres, and complicated firing cycles are among the numerous means that have been employed to control the burnout of organic compounds, decrease the combustible concentrations in the kiln atmosphere, and reduce the thermal stresses differential shrinkage and high cracking frequency. These methods however, require expensive and sophisticated equipment and increase the cost of firing.

[0007] In light of the foregoing problems experienced in the art, there remains a need for a method of fabricating and firing ceramic articles processed from batch mixtures containing oil-based compounds to form ceramic honeycomb structural bodies exhibiting less cracks, in a cost-effective and efficient manner.

SUMMARY OF THE INVENTION

[0008] In accordance with one aspect of the present invention, there is provided an improvement in a process of forming ceramic articles comprising oil-based components or extrusion aids, the improvement including removing the oil-based components after drying and prior to firing by flowing a heated gas through the green ceramic honeycomb articles to evaporate the oil-based components. Following evaporation, the gas is cooled to allow for condensation and isolation of the oil-based components.

[0009] Accordingly the practice of the invention involves forming a mixture of components comprising inorganic ceramic powder materials, a binder, a solvent for the binder, and, an oil-based component (hereinafter referred to as oil) having a flash point or ignition temperature; mixing and plasticizing the components to form a plasticized mixture; shaping the plasticized mixture into a green ceramic article; drying the green ceramic article; removing at least 70%, preferably at least 85%, and more preferably at least 95% of the oil from the dried green ceramic article by flowing a heated inert gas through the green ceramic

article; and, firing the green ceramic article substantially absent the oil to develop the product structure.

[0010] The heated gas is flowed at a rate of 2 to 10 standard cubic feet per minute (scfm) per 90 cubic inches of green ceramic article, preferably at a rate of 4 to 8 scfm. The gas may be air or a processed gas, such as nitrogen (N_2). The gas is used at a temperature which heats the green ceramic article to just below the flash point of the oil-based component contained therein. The flash point is the temperature at which vapor given off will ignite when an external flame is applied under specific test conditions. For example, if the oil has a flash point of 160°C, then preferably the gas has a temperature of between 110°-165°C, more preferably between 120°-140°C when the gas is air, and between 155°-160°C when the gas is N_2 .

[0011] In accordance with another aspect of the invention, there is provided an apparatus for removing oil-based components from green ceramic articles. The apparatus comprises a heating chamber for receiving the green ceramic articles and removing the oil-based components therefrom; a heat source coupled to an inert gas source for introducing a heated inert gas into the heating chamber; and, a heat exchanger coupled to a condensation chamber for collecting the removed oil-based components. Optionally, the apparatus further includes an adjustable microwave source, which may be operated at a power level of up to 400 watts per 90 cubic inches of ceramic article, preferably 100 Watts.

[0012] The heating chamber comprises a device for receiving and supporting the green ceramic articles. In one embodiment the device comprises a perforated base and a plate overlaying the base, the plate comprising a first end and a second end, and a set of holes sized to fit the ceramic articles, the holes extending from the first end to the second end of the plate, the holes being in communication with the perforated base. In another embodiment the device comprises a base having a first end and a second end, and a set of grooves cut into the base adjacent the first end but not extending to the second end, the set of grooves sized to the dimensions of the ceramic articles, each groove further having a plurality of holes extending through the second end of the base.

[0013] In still another embodiment the heating chamber comprises a plurality of devices for receiving and supporting the green ceramic articles, the devices arranged vertically in the heating chamber. Preferably the heating chamber is maintained at a pressure of 100 kPa to 130 kPa.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] The invention may be further understood by reference to the drawings wherein:

[0015] FIG. 1 is a block diagram of an apparatus illustrating one embodiment of the invention.

[0016] FIG. 2 is a block diagram of an apparatus illustrating another embodiment of the invention.

[0017] FIG. 3 is a cross-sectional view of an embodiment of a device for supporting ceramic articles in the process of the present invention.

[0018] FIG. 4 is a cross-sectional view of another embodiment of a device for supporting ceramic articles in the process of the present invention.

DESCRIPTION OF THE INVENTION

[0019] There is provided an improvement in the process of making ceramic multicellular articles, in particular ceramic honeycomb structures comprising oil-based components or extrusion aids. The improvement resides in removing oils from the green ceramic articles after drying and prior to firing to avoid uncontrolled burning and hazardous conditions during firing. This is achieved by flowing a heated inter gas through the green ceramic articles at a temperature, flow rate and time, sufficient to remove at least 70%, more preferably at least 85%, and most preferably at least about 95%.

[0020] The invention is applicable to ceramic powder processing which includes the formation of shaped articles from inorganic raw material powders and organic compounds. However, the invention is particularly suitable to the formation of ceramic articles which contain cordierite, and/or mullite. Examples of such mixtures being 2% to 60% mullite, and 30% to 97% cordierite, with allowance for other phases, typically up to 10% by weight. Some ceramic batch material compositions for forming cordierite that are especially suited to the practice of the present invention are those disclosed in U.S. patent 3,885,977 which is herein incorporated by reference in its entirety.

[0021] One composition which ultimately forms cordierite upon firing is as follows in percent by weight: 33% to 41%, and most preferably 34% to 40% of aluminum oxide, 46% to 53% and most preferably 48% to 52% of silica, and 11% to 17%, and most preferably 12% to 16% magnesium oxide. Suitable cordierite-forming inorganic ceramic powder raw materials

for the purpose of forming cordierite-containing ceramic articles may be selected from any source, and preferably include high-purity clay, talc, silica, alumina, aluminum hydroxides, and magnesia (MgO)-yielding raw materials. The preferred inorganic ceramic raw materials include kaolinite clay, talc, and alumina.

[0022] Types of clay are non-delaminated kaolinite raw clay, such as Hydrite MP™ clay, or Hydrite PX™ clay, delaminated kaolinite, such as KAOPaque-10™ (K10) clay, and calcined clay, such as Glomax LL™. All of the above named materials are sold by Dry Branch Kaolin. Some typical kinds of talc are those having a surface area of about 5-8 m²/g, such as supplied by Barretts Minerals, under the designation MB 96-67™. Some typical aluminas are coarse aluminas, for example, Alcan C-700 series, such as C-701™, or fine aluminas such as A-16SG™ from Alcoa. One typical kind of silica is that having a particle size of about 9-11 micrometers, and a surface area of about 4-6 m²/g, such as IMSIL™ sold by Unimin Corporation.

[0023] In filter applications, such as in diesel particulate filters, it is customary to include a burnout agent in the mixture in an amount effective to subsequently obtain the porosity required for efficient filtering. A burnout agent is any particulate substance (not a binder) that burns out of the green body in the firing step. Some types of burnout agents that can be used, although it is to be understood that the invention is not limited to these, are non-waxy organics that are solid at room temperature, elemental carbon, and combinations of these. Some examples are graphite, cellulose, flour, etc. Elemental particulate carbon is preferred. Graphite is especially preferred because it has the least adverse effect on the processing. In an extrusion process, for example, the rheology of the mixture is good when graphite is used. Typically, the amount of graphite is about 10% to about 50%, and more typically about 15% to about 30% by weight based on the powder material.

[0024] The inorganic ceramic raw materials are combined with organic compounds which according to the present invention include but are not limited to binders, lubricants, surfactants, and the like. In a preferred embodiment the organic compounds include an oil or oil-based compound, a binder, and optionally other organic processing aids such as surfactant. A solvent for the binder is also provided which may or may not be an organic.

[0025] Suitable oil or oil-based compounds in the formation of cordierite ceramic articles according to the present invention are low molecular oils (e.g., Durasyn® 162 HP polyalpholefin, available from Amoco Chemicals). A binder acts to bind the inorganic

powders and impart plasticity to the batch when mixed with a solvent. Especially useful in the practice of this invention are cellulose ether binders, such as methylcellulose, and/or methylcellulose derivatives. A solvent for the binder is provided to dissolve the binder, and further provide plasticity to the batch and wetting of the powders. The solvent can be aqueous or organic-based, which is normally water or another water-miscible solvent. For cellulose ether binders, the solvent is water. The surfactant, if present, promotes emulsification between the solvent and oil. Some surfactants that can be used in the practice of the present invention are stearic acid, oleic acid, and combinations of these.

[0026] The inorganic raw materials are mixed together with the organic compounds and solvent to form a plasticized batch mixture. In a preferred embodiment, the batch composition comprises 100 parts by weight of inorganic powder raw materials, 4 to 10 parts by weight of the oil, 2 to 5 parts by weight of the binder, 0.2 to 1 parts by weight of the surfactant, and 8 to 25 parts by weight of the solvent.

[0027] Batch formation takes place in two stages prior to the shaping step. In the first stage or wetting stage of batch formation, the inorganic powder particles, surfactant (if present), and the binder component are dry mixed followed by addition of the solvent such as in a Littleford mixer. The solvent is added in an amount that is less than is needed to plasticize the batch. The powder particles are coated and dispersed by the surfactant, solvent, and oil. In a second stage the plasticization takes place. In this stage the wet mix from the first stage is sheared in any suitable mixer in which the batch will be plasticized.

[0028] The resulting plasticized batch is then shaped into a green structural body by any known method for shaping plasticized mixtures, such as e.g. extrusion, injection molding, slip casting, centrifugal casting, pressure casting, dry pressing, and the like. The invention is best suited for extrusion through a die. The extrusion operation can either vertical or horizontal, can be done using a hydraulic ram extrusion press, or a two stage de-airing single auger extruder, or a twin screw mixer with a die assembly attached to the discharge end. In the latter, the proper screw elements are chosen according to material and other process conditions in order to build up sufficient pressure to force the batch material through the die.

[0029] The ceramic articles of this invention can have any convenient size and shape and the invention is applicable to all processes in which plastic powder mixtures are shaped. The process is especially suited to the production of cellular monolith bodies such as honeycombs. Cellular bodies find use in a number of applications such as catalytic,

adsorption, electrically heated catalysts, filters such as diesel particulate filters, molten metal filters, regenerator cores, and the like.

[0030] The green ceramic structural bodies are dried according to conditions well known in the art, and thereafter are fired according to conditions described as follow. Organic materials of the type described above are typically removed from green ceramic bodies in the temperature region of about 100°-600°C. The major obstacle in using mixtures with organics is that the articles crack when fired, particularly in very thin wall honeycomb structures. The cracking is a result of internal stresses developed during the removal of large amount of organics which causes excessive temperature or pressure gradients internal to the bodies. Furthermore, the fast release of organics over a narrow temperature range can produce dangerously high concentrations of combustible compounds in the kiln atmosphere and potentially explosions.

[0031] Following drying and prior to firing, a portion of the oil is removed so as to avoid uncontrolled burning and hazardous conditions during manufacturing. Removal is accomplished by forcing heated gas, with or without microwave heating, at a desired velocity through ceramic articles to evaporate the oil-based non-solvent component. Preferably at least 70%, more preferably at least 85%, and most preferably at least about 95% of the oil-based non-solvent component is removed.

[0032] One embodiment of the present invention is shown in FIG. 1 as a block diagram of an apparatus. This apparatus comprises a processing chamber **10** configured to receive a mass of ceramic ware **12** positioned vertically on a support device **32**. A gas system **14** is coupled, directly or indirectly, to the processing chamber **10**. The gas system **14** comprises a gas source **16**, a heater **18** for heating the gas and a fan or pump **20** for controlling the velocity of the gas. The gas system **14** is further connected to a gas system controller **22** for controlling the velocity and temperature of the gas. The gas system controller **22** in turn is in communication with the processing chamber **10** through a temperature measurement system **30** such as a thermocouple. The temperature measurement system **30** is preferably placed at a desired distance above the ceramic ware **12**.

[0033] The processing chamber **10** is further coupled to a heat exchanger **24** which acts to cool the hot gas from the processing chamber **10** to a temperature sufficient to allow for condensation of the oil-based non-solvent in the condensation chamber **26**. An exhaust system **28**, which acts to evacuate the cooled gas free of the condensed oil-based non-solvent,

is preferably in communication with the condensation chamber **26**. In an alternate embodiment the condensed oil-based non-solvent is reused in the ceramic batch forming components. In an additional embodiment a recirculation system (not shown) could take the place of the exhaust system **28**, and recirculate the gas.

[0034] A gas for purposes of the present invention is either air or a non-reactive gas. Cost-wise air is preferred. A suitable non-reactive gas is nitrogen (N_2), especially when the process temperature is close to the flash point of the oil. In operation hot gas is forced at a desired velocity by fan or pump **20** through gas inlet ducts (not shown) into the processing chamber **10** downward through the longitudinal cells of ceramic ware **12**, the direction which as indicated by arrows **34**. The hot gas uniformly heats the ceramic ware **12** in order to effect efficient removal of the oil.

[0035] The temperature and velocity of the gas supplied to the ceramic ware **12** is controlled by gas system controller **22** which operates the heater **18** and fan or pump **20**. The gas system controller **22** is coupled to a temperature measurement device **30**, such as a thermocouple, which is in direct contact with the interior of processing chamber **10**. A suitable gas velocity or flow rate for the purposes of the present invention ranges between 0.2 and 8 standard cubic feet per minute (scfm) per 90 cubic inches of green ceramic ware **12**. The gas flow depends on the wall thickness of the honeycomb structure being processed. Generally, the thicker the walls the slower the rate employed. It is preferred to utilize a gas flow rate of between 4 and 8 scfm. The temperature of the gas is sufficient to heat the ceramic article to a temperature below the flash point of the oil contained therein. Gas temperatures of between 110° and 165°C have been successfully utilized to remove an oil with a flash point of 160°C, although preferably the air temperature is between 120° and 140°C, and closer to 160°C when the gas is N_2 .

[0036] After flowing through the ceramic ware **12**, the hot gas carrying the oil exits the processing chamber **10** through gas outlet ducts (not shown) and enters the heat exchanger **24** where it is cooled off. From the heat exchanger **24**, the now-cooled gas reaches the condensation chamber **26** where the oil is condensed into a liquid by means known in the art. The hot gas prevents condensation of the removed oil back on the ceramic ware **12** or on the heating chamber **10**, thus allowing for a safe efficient process. In operation the removal of the oil involves evaporation, with subsequent condensation, but not burning-off. The dangers associated with burning of oil components during firing found in the prior art, are therefore

minimized and substantially eliminated. It has been found that the removal process according to the present invention does not affect the properties of the product.

[0037] The recovered oil can be periodically evacuated through the condensation chamber **26** through an exit or drain (not shown). It is also contemplated that the recovered oil may be for its intended purpose as discussed in the forming processing steps above. When using a gas other than air, a cost effective measure is to recirculate the gas. In such an instance a recirculation system (not shown) would replace the exhaust system, the recirculation system being coupled to the gas system. The heating chamber **10** is preferably maintained at a pressure of about 100 kPa to 150 kPa and at a temperature above 120°C.

[0038] In another embodiment, microwave power is utilized in order to effect faster heating of the ceramic ware. Referring now to FIG. 2 therein shown is another embodiment of the present invention as a block diagram of an apparatus. This apparatus is similar to the apparatus of FIG. 1, with the addition of a microwave system **36** coupled directly or indirectly, to the processing chamber **10**. In this embodiment processing chamber **10** is also a cavity resonator. The microwave system **36** comprises a microwave generator or source **38** and a microwave controller **40**. The microwave generator **38** is coupled to the processing chamber **10** by any suitable means, such as waveguides **42**. The microwave controller **40** which functions to control the microwave generator **38** is in communication with inside of the processing chamber **10** through temperature measurement **44** located below the ceramic ware **12**.

[0039] The microwave source employed to generate the microwaves can comprise any conventional magnetron with an adjustable power feature. Preferably, the frequency of incident microwave used should be greater than 800 MHz, preferably between about 915 MHz or 2.45 GHz, which are designated industrial band in the United States. Furthermore, the power of the incident microwave need be no greater than that sufficient to, as described above, heat the ceramic articles to the desired temperature. Specifically, the microwave power source should possess variable power levels ranging between 1 to 75 kW. The microwave controller is standard such as those known in the industry and comprises one or more solid state devices capable of achieving the desired control of the power of the microwave energy delivered to the processing chamber. The microwave power is operated at levels of up to 400 Watts (W) per 90 cubic inches of green ceramic ware, most preferably at 100 W.

[0040] In setting up the parameters or setpoints necessary for determining the necessary gas temperature and velocity, as well as microwave radiation, to remove a portion of oil components in a reasonable time, factors including the ceramic composition, geometry, capabilities of the equipment should be considered. For example, a cordierite honeycomb body exhibiting a 7 in. length, a diameter of 3.866 in., a 2.8 mil cell wall thickness and a cell density of 900 cell/in² is heated in N₂ for 35 minutes to about 160°C, at a gas flow rate of about 6.0 scfm, with no hold, followed by a 15 minute cool down to about 100°C. For a similar product, with the microwave radiation of 100 Watts, the ceramic ware is heated for 6 minutes to about 160°C at a flow rate of 4.0 scfm, with a hold of 6 minutes at top temperature, followed by a 5 minute cool down to about 100°C. In another example, a diesel particulate substrate, comprising a cordierite honeycomb body having a length of 4.7 in., a diameter of 5.66 in., a 20 mil wall thickness, and a cell density of 200 cell/in² is heated in N₂ for 60 minutes to about 150°C, at a gas flow rate of about 1.5 scfm, with a hold of 1 hour at top temperature, followed by a 15 minute cool down to about 100°C.

[0041] The processing chamber **10** is configured to receive a mass of ceramic ware **12** which could either be arranged to be stationary or continuously passed therethrough. A support device, having a shelf-like design, is employed to receive and hold a plurality of ceramic ware. An embodiment of a suitable support device **32** is shown in cross-section in FIG. 3 and comprises a base **50** and a detachable plate **52**. Base **50** comprises a plurality of perforations **54** which extend from a top end **56** to a bottom end **58**. The design of base **50** is such to allow the heated gas to flow therethrough. A plate **52** overlays base **50**, and comprises a first plate surface **60**, a second plate surface **64**, and a set of holes **66** extending therebetween. The holes **66** are in communication with the perforated base **50**, and sized to receive and support the ceramic articles being processed. Holes **66** are smaller than the received ceramic ware. The number of ceramic articles arranged on the plate **52** is not significant in the practice of the present invention. Plate **52** may be interchanged with similar members depending on the dimensions and number of ceramic articles being processed in a given cycle. The ceramic articles **12** are arranged on support device **32** vertically in order to effect the flow of the heated gas longitudinally through the cell channels of the honeycomb structure.

[0042] Referring now to FIG. 4 therein shown is another embodiment of a support device **32** for suitable for receiving and holding a mass of ceramic ware **12** for processing according

to the present invention. The support device **32** comprises a base **70** having a top end **72**, a bottom end **74**, and a set of apertures **76** cut adjacent to the top end **72**, but not extending to the bottom end **74**. The set of apertures **76** are sized to the dimensions of the ceramic articles **12**. Each aperture **76** further includes a plurality of perforations **78** extending through the bottom end **74** for the heated gas to flow therethrough, and a lip **80** along the periphery of each aperture for supporting the ceramic article **12** a distance above the perforations **78**, to encourage efficient gas flow.

[0043] It is envisioned that in one embodiment the processing chamber comprises a plurality of such support devices mounted vertically the length of the processing chamber. In another embodiment the processing chamber comprises one support device which is either stationary or continuously moving.

[0044] Following the removal of the oil, the prepared ceramic bodies, still green, are then fired at a selected temperature under suitable atmosphere and for a time dependent upon the composition, size and geometry so as to result in a fired body of the desired ceramic. The invention is not limited to specific firing temperatures and times. For example, in compositions which are primarily for forming cordierite, the temperatures are typically from about 1300°C to about 1450°C, and the holding times at these temperatures are from about 1 hour to about 8 hours. For mixtures that are primarily for forming mullite, the temperatures are from about 1400°C to about 1600°C, and the holding times at these temperatures are from about 1 hour to about 6 hours. For cordierite-mullite forming mixtures which yield the previously described cordierite-mullite compositions, the temperatures are from about 1375°C to about 1425°C. Firing times depend on factors such as kinds and amounts of materials and nature of equipment but typical total firing times are from about 20 hours to about 80 hours.

[0045] There are numerous benefits associated with the present method of removing oil-based components and forming ceramic bodies. By removing the oil-based components prior to firing, the green ceramic bodies can be fired faster and more safely. The stringent requirements of controlling the kiln atmosphere during firing of green ceramic bodies containing oil-based non-solvent is eased in the instant invention allowing firing in conventional kilns and reducing manufacturing costs. Further, already existing forming and manufacturing processes can be utilized.